Enhancing the UV-protection and Antibacterial Properties of Polyamide-6 Fabric by Natural Dyeing

Nabil A. Ibrahim[1], Wessam M. El-Zairy[2], Mohammed R. El-Zairy[2], Heba A. Ghazal[2]

[1]National Research Centre, Textile Research Division, Dokki, Cairo, Egypt

[2] Faculty of Applied Arts, Printing, Dyeing and Finishing Dept. Helwan Univ., Cairo, Egypt

nabibrahim49@yahoo.co.uk

Abstract

There is an increasing interest in adding value to polyamide-6 fabrics via upgrading their functional properties. In the present study, selected natural dyes namely madder and safflower yellow dyes as well as an eco-friendly mordants namely alum, Zn-sulfate and tannic acid have been used to identify the proper dyeing conditions for attaining high quality natural dyeings along with imparting multifunctional properties, i.e. UV-protection and anti-bacterial properties, to the dyed polyamide- 6 fabric. The results demonstrate that the improvement in dyeing properties, i.e. color yield as well as fastness properties, along with the enhancement in the imparted functional properties are governed by the type and concentration of natural dye, kind of mordant, dyeing sequence and conditions. The dyes/ mordants examined exhibited high fastness properties and offered better UV-protection function and antimicrobial activity against G-ve bacteria (*E-coli*) and G+ve bacteria (*S. aureus*).

Keywords

Polyamide-6; Natural dyes; Mordants; UV-protection; Anti-microbial

Introduction

Recently, there has been a growing interest in using the non-toxic, eco-friendly coloring materials for textile coloration to avoide and/or minimize the negative impacts of intermediates, auxiliaries as well as chemicals used in synthetic dyes [1-2]. Accordingly there is a great potential for using natural dyes in textile applications instead of the synthetic ones taking into consideration the environmental concerns and technical drawbacks of natural dyes [3-5] Applications of natural dyes from plant sources is preferable because of their very low toxicity. To overcome low exhaustion, low fixation and poor fastness properties of natural dyeings, as well as to develop different shades with the same dye, attempts have been focused on the use of mordants such as metalic mordants, e.g. alum, zinc-salts, copper-salts, iron-salts…etc., or natural mordants, e.g. tannins [6,7]. Pre-, meta, and post-mordanting have been practised for getting natural dyeings with better depth of shades, improved fastness properties and in different colors [6,7]. Both the natural dyes with ligands such as -OH, -NH_2, -COOH groups, and the textile fibers with active sites such as –NH_2, -COOH groups can make a complex with a metal ion of the metalic mordant thereby enhancing the extent of fabric-mordant-dye interactions [8,9].

On the other hand, some of previous studies have demonstrated that certain natural dyes such as Madder and Safflower yellow are able to add UV-protective and/or antimicrobial effects to textile materials [10-14].

The current research work examines the impact of both the type of natural dye as well as the kind of low environmentally impact mordant on enhancing the functional i.e. UV-protection and antibacterial activity, and dyeing properties of polyamide-6 fabric.

Experimental

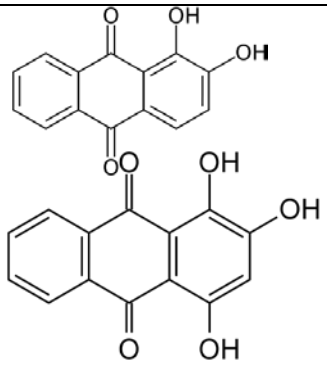
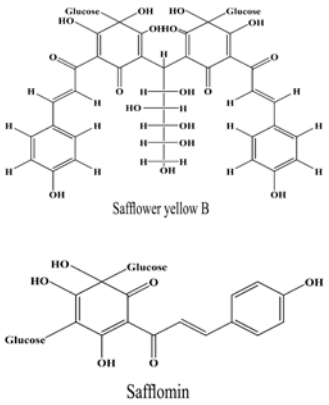
Materials

Mill-scoured and bleached knitted polymide-6 fabric of 58g/m^2 was used in this study. Commercial-grade natural dyes were purchased from local market.

Table 1 shows the chemical structures of the commercial natural dyes used in the experiment.

Albegal® B (a leveling agent, based on ethoxylated fatty acid amide derivatives, Ciba) and laboratory reagent-grade chemicals such as Zn-sulfate, alum, tannic acid, acetic acid and hydrochloric acid were used for the dyeing of polymide-6 with the nominated natural dyes.

TABLE 1 NATURAL DYES USED

Natural dye	Chemical structure
1. Madder [13]	Aliz arin  Pupurin
2.Safflowe r yellow dye [14]	 Safflower yellow B Safflomin

Methods

1) Properties of Colorants:

The used natural colorants were extracted from their dried-powder forms in a material-to-liquor ratio (LR) of 1/100 in distilled water at the boil for 2hrs. The cooled-extracted dye solutions were used as stock solutions after filtration.

2) Dyeing

Pre-mordanting, using Zn-sulfate [$ZnSO_4.7H_2O$], alum [$Al_2K_2(SO_4)_4$] or tannic acid as a mordant, was done at a temperature of 90°C, LR (1/30); time (30 min.) in the presence of the used mordant (3% owf). The premordanted samples were thoroughly rinsed in water and dried at 80°C/5min.

Dyeing of the pre-mordanted fabric samples was carried out at (60°-90°C), for (30-60 min.) in presence of Albegal® B (2% owf) as levelling agent, using 1/30 LR at different pH's. The dyeing temperature was raised at a heating rate 2°C/min to avoid unlevelness. After dyeing, the samples were soaped at 60°C for 15 min and thoroughly rinsed in water. Both pre-mordanting and subsequent natural dyeing were carried out in the shaking water bath. Typical formulations used in this study are given in the text.

3) Testing

Color strength, K/S of the obtained natural dyeings was measured and evaluated at the λ max of the used natural dye, using the color-Eye 3100® spectrophotometer and the Kubelka- Munk equation: $K/S = (1-R)^2/ 2R$ (where K: absorption coefficient, S: scattering coefficient, and R: reflectance) [15]

Fastness properties to washing, crocking and perspiration were assessed according to AATCC test methods (61-1972), (8-1972) and (15-1973) respectively.

UV-protection factor (UPF) was assessed according to the Australian/ New Zealand standard (AS/NZS 4399-1996).

Antimicrobial properties of the obtained natural dyeings against Gram- negative bacteria (*E*-coli) and gram positive bacteria G+ve (*S. aureus*) were examined for a clear zone of inhibition according to AATCC 100-1999.

Results and discussion

All in this article, attempts have been made to examine the suitability of using natural dyes in the dyeing of pre-mordanted polyamide-6 fabric, taking into consideration the environmental aspects, as well as to study the anti-microbial and UV-blocking properties of the obtained dyeings. Results obtained along with their appropriate discussion are as follows.

1) Dyeing Temperature

For a given set of pretreatment and subsequent natural dyeing conditions, Fig. 1 illustrates that: i) raising the dyeing temperature from 60° up to 90°C results in an improvement in the color depth, K/S, of the obtained madder (Fig. 1.a) and safflower- (Fig. 1b) dyeings, reflecting the positive impact of increasing the dyeing temperature on reducing the conglomeration of colorants molecules, enhancing the swellability of the pre-mordanted substrate, and increasing the accessibility and availability of the dye-sites [12,14] and ii) the extent of improvement is determined by the type of the natural dye, as well as kind of mordant: Zn-sulfate > alum > tannic acid, regardless of the used natural dye, and differences among them in their tendency to form quite strong bonds with both the dye ligands and the nylon-6 active sites [1,2,4,9,12]. The

given results signify that nylon-mordant-dye interactions are better and stronger in case of using Zn-mordant thereby resulting in darker depth of shade and higher K/S values

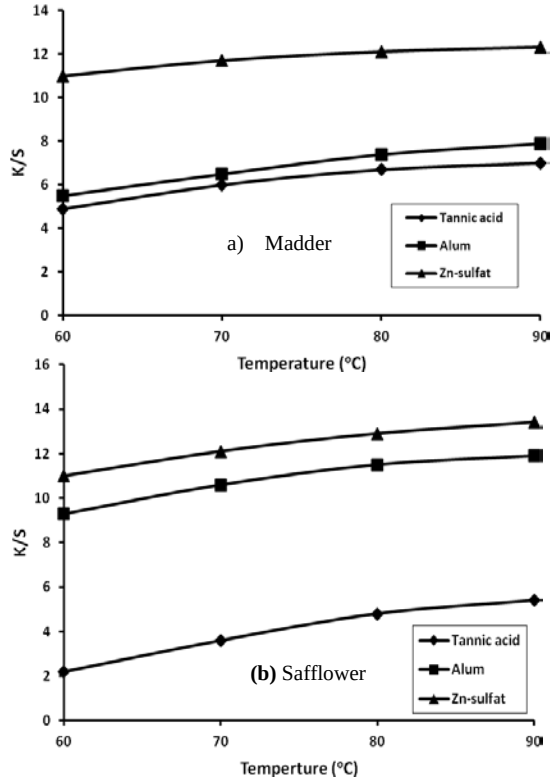


FIG. 1 EFFECT OF DYEING TEMPERATURE ON THE K/S VALUES OF THE OBTAINED MADDER-DYEINGS (FIG. 1A) AND SAFFLOWER-DYEINGS (FIG. 1B) PRE-MORDANTING CONDITIONS: MORDANT (3% OWF) AT 90°C FOR 30 MIN., LR (1/30). NATURAL DYEING CONDITIONS: DYE STOCK SOLUTION (50%); LEVELING AGENT (2% OWF); LR (1/30), TIME (60 MIN.); PH (2)

2) Dyeing Time

The obtained data, Fig. 2, showed that prolonging the dyeing time of premordanted substrates is accompanied by an increase in the extent of dye uptake as well as the color depth of the obtained madder (Fig. 2a) and safflower (Fig. 2b) dyeings regardless of the used mordant, as a direct consequence of enhancing the extent of diffusion, penetration as well as fixation of the disaggregated dye molecules onto and/or within the available dye sites of the swelled substrate.

3) Dye Concentration

It is clear, Fig. 3, that increasing the dye extract % from 0 up to 100% results in a sharp increase in the color depth of the obtained madder (Fig. 3a) and safflower (Fig. 3b) dyeings, due to the greater availability and accessibility of dye molecules onto and/or within the vicinity of easily accessible attachment sites [12,14].

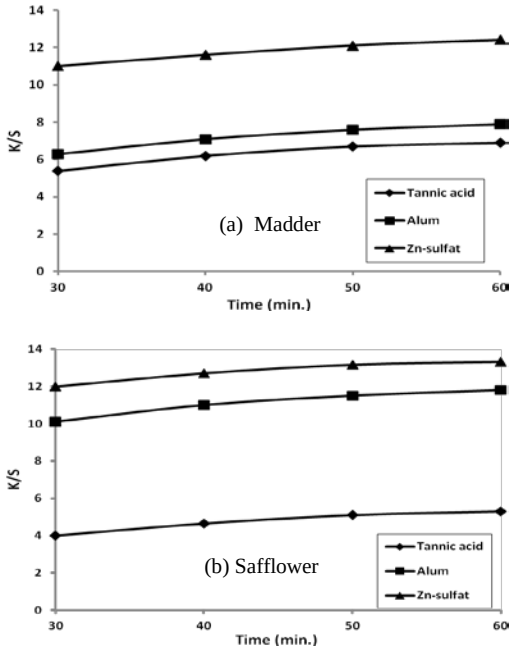


FIG. 2 EFFECT OF DYEING TIME ON THE K/S VALUES OF THE OBTAINED MADDER-DYEINGS (FIG. 2A) AND SAFFLOWER-DYEINGS (FIG. 2B) PRE-MORDANTING CONDITIONS: MORDANT (3% OWF) AT 90°C FOR 30 MIN., LR (1/30). NATURAL DYEING CONDITIONS: DYE STOCK SOLUTION (50%); LEVELLING AGENT (2% OWF); LR (1/30), AT 90°C; PH (2)

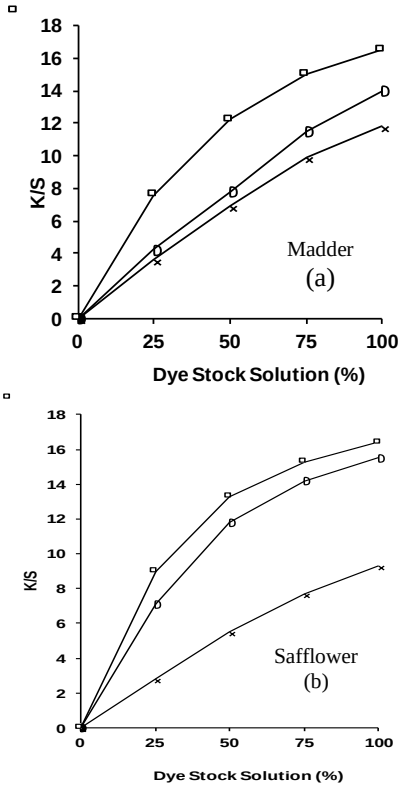


FIG. 3 EFFECT OF DYEING STOCK SOLUTION ON THE K/S OF THE OBTAINED MADDER-DYEINGS ((FIG. 3B). ZN-SULFATE (□); ALUM (●); TANNIC ACID (×). PRE-MORDANTING CONDITIONS: MORDANT (3% OWF) AT 90°C FOR 30 MIN., LR (1/30). ATURAL DYEING: LEVELLING AGENT (2% OWF); LR (1/30), AT 90°C FOR 60 MIN.; PH(2)

4) Dyeing pH

Figs 4a and 4b show that: i) the enhancement in K/S values of the obtained natural dyeings is determined by the pH of the dyeing bath and follows the decreasing order: pH2 (using hydrochloric acid)> pH6 (using acetic acid) regardless of the used natural dye, and ii) this enhancement in K/S values at pH2 may be attributed to better dye uptake and building up of natural dye molecules onto the protonated active sites of polyamide-6, i.e. amino (-NH_2) and amido (-CONH-), and the behavior of the used natural dyes like disperse dyes under the used acidic pH, thereby giving higher dye uptake, cannot be ruled out [4,16-17].

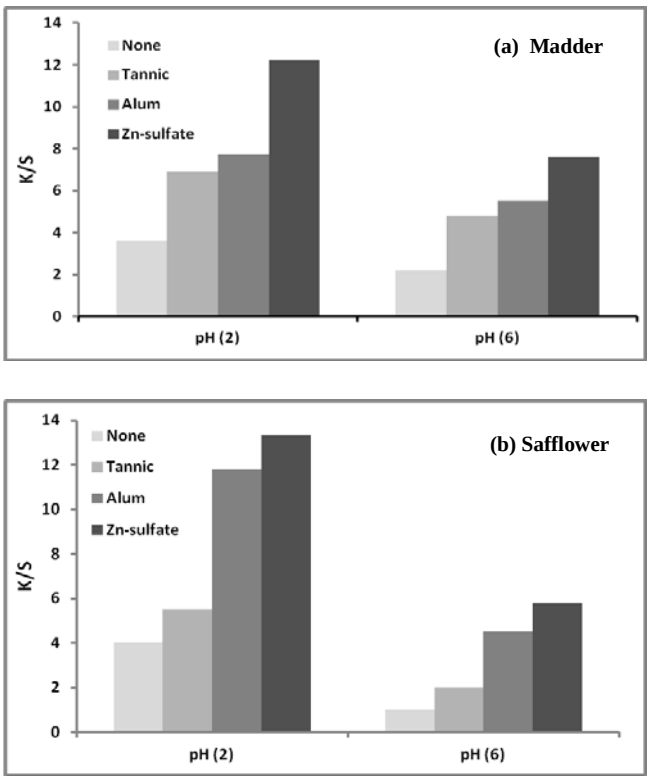


FIG.4. EFFECT OF THE DYEING BATH PH ON THE OBTAINED MADDER-DYEINGS (FIG. 4A) AND SAFFLOWER-DYEINGS (FIG. 4B) PRE-MORDANTING: MORDANT (3% OWF); AT 90^{O}C FOR 30 MIN, LR (1/30).NATURAL DYEINGS: DYE STOCK SOLUTION (50%); LEVELING AGENT (2% OWF); LR (1/30), AT 90^{O}C FOR 60 MIN

5) Functional and Dyeing Properties

As far as the changes in the dyeing and functional properties of the obtained natural dyeings as a function of kind of natural dye as well as type of mordant, the data in Table 2 signify that: i) premordanting using the nominated mordants brings about a remarkable improvement in the K/S of the obtained dyeings regardless of the used natural dye and mordant, ii) the extent of improvement in K/S value as well as fastness properties of the obtained natural dyeings is governed by the nature of the dye as well as the efficiency of the used mordant as discussed before, iii) pre-mordanting followed by natural dyeing results in an improvement in both the UV-protection properties against the harmful UV-B radiation as well as in the antibacterial activity against G-ve bacteria (*E*-coli) and G+ve bacteria (*S. aureus*), iv) the improvement in the UPF of pre-mordanted fabric samples is the most probably attributed to the formation of deeper shade and the more light absorption characteristics of the natural dye-mordant complex [11,8,18], and v) the increase of anti-microbial activity of pre-mordanted fabric samples reflects the inhibiting effect of the mordant, natural dye and/or both of them synergistically via binding the microbial proteins, [11,12] ability to reduce microbial growth [10], as well as may be the ability of the used mordants to inhibit or inactivate the cell [19], and vi) the inactivation of G+ve bacteria was more efficient than G-ve bacteria which reflects their differences in cell wall structure, outer membrane and in amenability to inhibition [20].

TABLE 2 DYEING AND FUNCTIONAL PROPERTIES OF OBTAINED NATURAL DYEINGS

Mordant	Natural dye	K/S	Fastness Properties								UPF	Z.I (mm)	
			WF		RF		PF						
							Acid		Alkali				
			St.	Alt.	Dye	Wet	St.	Alt.	St.	Alt.		G -ve	G +ve
None	None	--	--	--	--	--	--	--	--	--	12	0.0	0.0
	Madder	3.61	4-5	4-5	4-5	4	3-4	4	4	4	19	3.7	4.6
	Safflower	4.02	4-5	4-5	4-5	4	4-5	4-5	4-5	4-5	13	2.8	3.6
Alum	None	--	--	--	--	--	--	--	--	--	19	1.2	2.3
	Madder	7.72	5	5	4-5	4-5	4-5	4-5	4-5	4-5	25	8.0	9.1
	Safflower	11.81	5	5	5	4-5	4-5	4-5	4-5	4-5	22	5.0	6.2
Zn-Sulfate	None	--	--	--	--	--	--	--	--	--	27	5.0	5.8
	Madder	12.20	5	5	4-5	4-5	4	4-5	4	4-5	40	14.0	15.1
	Safflower	13.32	5	5	5	5	4-5	4-5	4-5	4-5	35	9.0	9.8
Tannic acid	None	--	--	--	--	--	--	--	--	--	23	3.4	4.5
	Madder	6.91	5	5	5	5	4	4-5	4	4-5	37	11.0	12.2
	Safflower	5.52	5	5	5	4-5	4-5	4-5	4-5	4-5	30	6.0	7.0

Pre-mordanting: mordant (3% owf); LR (1/30); at 90°C for 30 min.Natural dyeing: dye stock solution (50%); leveling agent (2% owf); pH(2); LR (1/30), at 90°C for 60 min.K/S: Color strength, WF: wash fastness; RF: rubbing fastness; PF: perspiration fastness; UPF: UV-protection factor; ZI: zone of inhibition.

Conclusions

This study was aimed to investigate the possibility of upgrading the functional properties of polyamide-6 fabric via natural dyeing. The multifunctionality of the obtained natural dyeings was evaluated by analyzing its UV-protection efficiency and antibacterial activity against G-ve bacteria (*E*-coli) and G+ve bacteria (*S. aureus*). The obtained results signified that

multifunctional properties can be obtained by post-dyeing of premordanted polyamide- 6 fabric, with alum, Zn-sulfate or tannic acid, as an eco-friendly mordant, with madder and safflower yellow natural dyes. The enhancement in K/S and fastness properties of the obtained dyeings as well as the improvement in the imparted UV-protection and anti-bacterial properties are determined by the type of both the natural dye and the used mordant.

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Nabil Abd El-Basset Ibrahim, born on April 11, 1949 in El-Mansoura, Egypt, obtained his PhD in Applied Organic Chemistry (Textile Finishing) in 1979. He is a Professor of Textile Chemistry and Technology, Textile Research Division NRC (from 1990 to 2007) and was the Head of the Textile Research Division NRC (August 13, 2001 to August 21, 2008). He has published over 214 scientific papers in well-known international journals dealing with textile chemistry and chemical technology, pollution prevention and cleaner production in textile industry, applications of biotechnology in textile wet processing, functional finishes of cellulose-based textiles for specific end uses using nanotechnology, bio-technology and plasma technology. He has implemented more than 45 industrial projects and supervised over 60 MSc and PhD theses. He has been an industrial and environmental auditor, and eco-textile consultant for several projects sponsored by foreign (EP3, SEAM, DANIDA, CIDA, FINIDA, BAT4MED) and local organizations. He was awarded the NRC Prize in Chemistry, for Scientific Contribution and Distinction in Chemistry and its Applications (1996), Professor Dr M.K. Tolba's Environmental Prize (1998) for 'The Best Applied Research for Protection of Air, Water and/or Soil', and State Prize of Distinction for Advanced Technological Science (2004). Two NRC prizes for Excellent Scientific Publications and patent (2009), Merit Prize of the NRC in Advanced Technological Sciences (2010), Merit Prize of the State in Advanced Technological Sciences (2010), NRC prize for Excellent Scientific Publications (2010), NRC prize for Excellent Scientific Publications (2011). He was the Chairman of the 1st (March, 2004), 2nd (April, 2005), 3rd (April, 2006) and 4th (April, 2007) International Conferences of the Textile Research Division (Textile Processing: State of Art and Future Developments), at NRC, Cairo Egypt. He was nominated by the International Biographic Center (IBC) as a listee of the IBC Leading Scientific of the World 2008. He is one of the leading scientists and engineers of OIC (Organization of Islamic Conference) Member States (COMSTECH's Study 2008). He was nominated by the International Biographic Center (IBC) as a listee of the TOP 100 SCIENTISTS for 2012. He is a reviewer for more than 30 international journals. He was one of the authors of Volume 2 "Handbook of textile and industrial Dyeing: Application of Dyes" for "Woodhead Publishing Limited, Cambridge, UK" ISBN 1 84569 696 4.

Mohamed Reda Abd El-Aziz El-Zairy, born on April 17, 1948 in Garbia, Egypt. Ph. D., Textile printing Technology, Faculty of Applied Arts, Helwan University (1985). He is professor at Textile Printing, Dyeing and Finishing Department, Faculty of Applied Arts, Helwan University (17/1/ 1996 - Until now) and was Head of Textile Printing, Dyeing and Finishing Department (9/6/2006-30/7/2008). He has published over 40 Papers in International and Local Journals in the Field of Textile Printing, Dyeing and Finishing and supervised 18 M. Sc. & Ph.D theses. E-mail: mohamedredaelzairy@yahoo.com.

Wessam Mohamed Reda Abd El-Aziz El-Zairy, born on September 7, 1978 in Garbia, Egypt. Ph. D., Textile printing Technology, Faculty of Applied Arts, Helwan University in 2006. She is Professor Assistant in Technology of Textile Printing, Dyeing and Finishing, Faculty of Applied Arts, Helwan University. She has published 12 Papers in International and Local Journals in the Field of textile Printing, Dyeing and Finishing. E-mail: wessam.reda@yahoo.com.

Heba Abdel Mohsen Ghazal, born on July 23, 1977. Ph. D., Textile printing Technology, Faculty of Applied Arts, Helwan University in 2011. She worked as Faculty Aide, Faculty of Applied Arts, Helwan University (2000-2003), and as production engineer in Helwan Factory for readymade garment. She is lectures in Higher Institute of Applied Arts. E-mail: Ghazal.heba@yahoo.com.